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## Effect of monoethanolamine concentration on CO<sub>2</sub> capture by poly (chloromethyl styrene) grafted fibrous adsorbent

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**ABSTRACT.** The CO<sub>2</sub> adsorption performance of poly (chloromethyl styrene) (PCMS) grafted on polyethylene coated polypropylene (PE/PP) fibrous polymer substrate and followed by amination with monoethanolamine (MEA) was investigated using gravimetric sorption system. The chemical, structural and morphological changes in the aminated adsorbents were evaluated using Fourier transform infrared spectroscopy (FTIR) and X-ray diffraction (XRD), respectively. The amination was carried out using three different compositions of MEA (50, 80 and 100%) diluted in water to optimize the yield of loaded amine. The highest percent of amination obtained was about 71% and the amine content increase with the rise in MEA concentration. The CO<sub>2</sub> adsorption capacity increase with MEA concentration with the highest capacity recorded was 1.63 mmol/g with pure CO<sub>2</sub> gas at 30 bars and room temperature.

### 1. Introduction

The development of technologies for the improvement of life style has increased the demand for more power production, which in return increases the usage of fossil fuels and subsequently increase the carbon dioxide (CO<sub>2</sub>) emission in the atmosphere [1]. It is reported that the content of CO<sub>2</sub> in atmosphere is predicted to exceed 500 ppm by 2020 if no urgent combating action taken [2]. This situation has raised the concern over the removal of the CO<sub>2</sub> from upstream to downstream of power production processes before releasing them to the atmosphere at the allowable concentration. This can eventually contribute to the reduction of the global warming and climate change in addition to minimization of the health risk such as respiratory illnesses and asthma [1,3,4]. Therefore, several technologies for CO<sub>2</sub> capture have been explored including chemical absorption, physical adsorption, cryogenic methods, membrane separation, and biological fixation [5]. However, chemical absorption process is generally recognized as the most effective and matured technology for CO<sub>2</sub> capture and the absorption is carried by alkanolamines such as monoethanolamine (MEA), diethanolamine (DEA) and methyldiethanolamine



(MDEA), all of which react with CO<sub>2</sub> forming carbamate that can be decomposed to regenerate the alkanolamines [6]. In fact, aqueous MEA solution is the most frequently used alkanolamines absorbent due to its high reactivity with CO<sub>2</sub>, low solvent cost, and can be regenerated easily [7,8]. Unfortunately, absorption with amine solutions is associated with equipment corrosion, high power consumption leading to high operational cost and poor overall thermal efficiency [9]. Alternatively, physical adsorption of CO<sub>2</sub> by porous adsorbents offers low energy consumption, ease of regeneration, and superior cycling capability [10]. Recent research efforts revealed new adsorbent materials such as ultrahigh porosity of metal organic framework (MOF) with very high CO<sub>2</sub> adsorption capacity that can reach 54.53 [11] and 58.15 mmol/g [12]. However, physical adsorption still has the disadvantage of lower CO<sub>2</sub> selectivity than chemical absorption in addition to processing issues including the pressure drop, dustiness, clogging, mass loss, challenges in handling and transportation, all of which hampered the industrial application of MOFs [13,14].

Therefore, chemical adsorption with amine-containing adsorbent is preferred as the performance can be sustained due to the strong bonding between the substrate and the CO<sub>2</sub> molecules itself leading to high CO<sub>2</sub> selectivity due to Lewis acid and Lewis base interaction [15]. Such strong bonding between amine groups and the adsorbent is important in minimizing the losses of amine during the adsorption and desorption cycles. Radiation induced grafting (RIG) is a facile method that can impart new chemical characteristics to polymer substrates. This is a promising modification technique because of its ability to permanently modify the substrate or adsorbent without changing their inherent properties [16,17]. Thus, this technique can be used to functionalize the inert polymer substrates with acrylic or vinyl monomers such as glycidyl methacrylate (GMA) or chloromethyl styrene (CMS), which is a conventionally known as vinylbenzyl chloride [18,19]. The objective of this study is to prepare fibrous adsorbent with different amine contents based on polyethylene coated polypropylene (PE/PP) by RIG of CMS monomer and the subsequent amination with different concentration of monoethanolamine (MEA). The CO<sub>2</sub> adsorption performance of the obtained adsorbents was investigated using gravimetric sorption system.

## 2. Materials and methods

### 2.1 Chemicals and Reagents

The bi-component fibers of polyethylene coated polypropylene (PE/PP) nonwoven sheet was grafted with poly(chloromethyl styrene) to yield grafted fibers (PE/PP-g-PCMS) following the procedure reported in literature [16] and has a degree of grafting of 137%. The irradiation dosage from electron beam was set at 100kGg for 2 hour of reaction with CMS concentration of 5wt% at 40 °C of temperature. MEA (purity ≥99%) was purchased from Merck and diluted to different concentrations (100, 70 and 50%) with deionized water (DI), which obtained from Barnstead Nanopure Diamond Lab Water Purification System (ThermoFisher, Waltham, USA). DI water was also used for samples washing purposes together with ethanol (purity of 99.6%) from Chemiz. Pure CO<sub>2</sub> (99.8%) and N<sub>2</sub> s (99.995%) gases were supplied by Linde Malaysia (Sdn Bhd) for sorption tests.

### 2.2 Apparatus and measurements

The changes in chemical composition after grafting and amination were analyzed using a Nicolet iS50 FT-IR spectrometer with spectra obtained in a frequency range of 500-4000 cm<sup>-1</sup> using 32 scans and 4 cm<sup>-1</sup> resolution. The crystalline structural changes of the samples were investigated by X-ray diffraction (XRD) using a PANalytical Empyrean analyzer at a Bragg's angle in the range of 5-70°. Both analysis was carried out using pristine, grafted PE/PP (PE/PP-g-PCMS) and aminated PE/PP (PE/PP-g-PCMS-MEA) samples. CO<sub>2</sub> adsorption capacity of the aminated samples were analyzed using a gravimetric sorption analyzers-isoSORP®, Rubotherm-TA instruments operated in a pressure range of vacuum to 30 bar and at 30 °C.

### 2.3 Amine Functionalization

A 0.1 g of PE/PP-g-PCMS was placed inside a 100 ml round bottom flask containing 30 ml of MEA solution. The reaction was carried out under reflux at 100 °C for 2 h of reaction. The MEA-functionalized substrates (PE/PP-g-PCMS-MEA<sub>x</sub>), where x refers to three different contents (loadings) of MEA amine MEA concentrations of 01=100%, 02 = 80% and 03 = 50% were used. The samples were removed and washed repeatedly with DI water and ethanol then dried at 60 °C for 5 hours. The weight changes in PE/PP-g-PCMS-MEA<sub>x</sub> samples were recorded before and after the reaction with an accurate weight balance to calculate the percentage of amination. The following equation was used to calculate the amine percentage:

$$\text{Percent of amination (\%)} = \frac{(W_a - W_g) / W_{MEA}}{(W_a - W_o) / W_{CMS}} \times 100\% \quad (1)$$

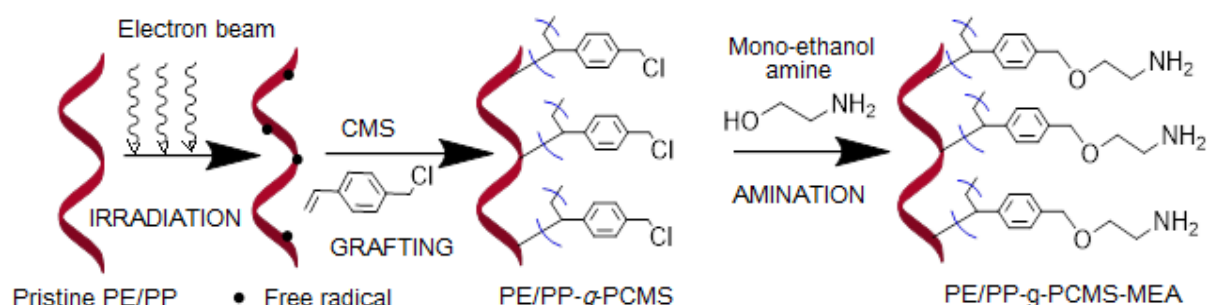
Where  $W_{CMS}$  and  $W_{MEA}$  are the molecular weights of CMS and MEA (g/mol), respectively.  $W_a$  and  $W_g$  are the weight (g) of the PE/PP-g-PCMS substrate before and after amination. The  $W_o$  is the weight of PE/PP substrate before grafting.

### 2.4 CO<sub>2</sub> adsorption tests

0.1 g of PE/PP-g-PCMS-MEA<sub>x</sub> substrates was placed inside the sample container and the adsorption equilibrium of carbon dioxide (CO<sub>2</sub>) were performed in a magnetic suspension balance (MSB) of gravimetric sorption analyser-isoSORP® from Rubotherm-TA instruments. Details of the basic principles, components and operational procedure of MSB was described elsewhere [20,21]. Pretreatment was carried out at temperature of 80°C for 2 h under vacuum condition to remove the moisture and impurities from the substrate followed by buoyancy measurements, which were performed at 30°C from vacuum up to 30 bar using purified nitrogen gas with a 500 ml/min flow rate. The last procedure was the adsorption equilibrium measurement, which was measured at 30°C from vacuum to 30 bar with a flowrate of 500 ml/min using pure CO<sub>2</sub>. This procedure was repeated to five samples including pristine PE/PP, PE/PP-g-PCMS, PE/PP-g-PCMS-MEA01, PE/PP-g-PCMS-MEA02 and PE/PP-g-PCMS-MEA03.

## 3. Results and discussion

Figure 1 shows a reaction scheme for grafting of CMS onto PE/PP using RIG method and subsequent amination with MEA. The adsorbent precursor was obtained by irradiation of PE/PP substrate with an electron beam to form free radicals. The irradiated samples were subsequently reacted with CMS monomer by replacement of chlorine originated from covalently bonded PCMS grafts [22].

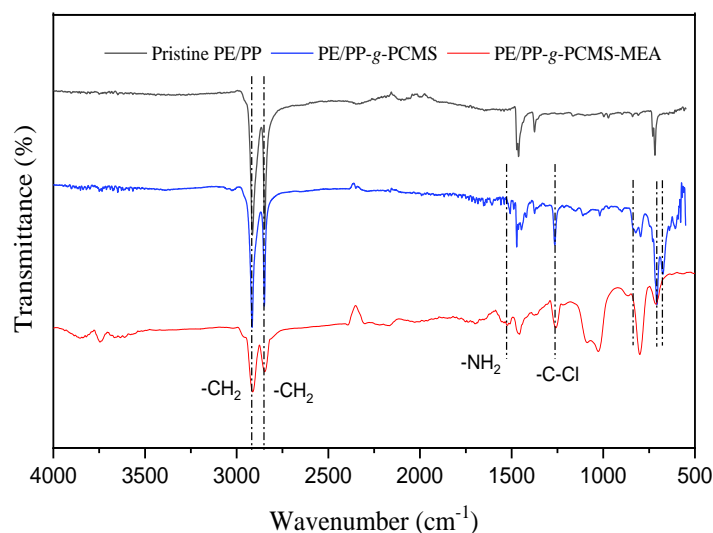


**Figure 1.** Reaction scheme for grafting of CMS onto PE/PP substrate and subsequent amination

### 3.1 Structural Characterization

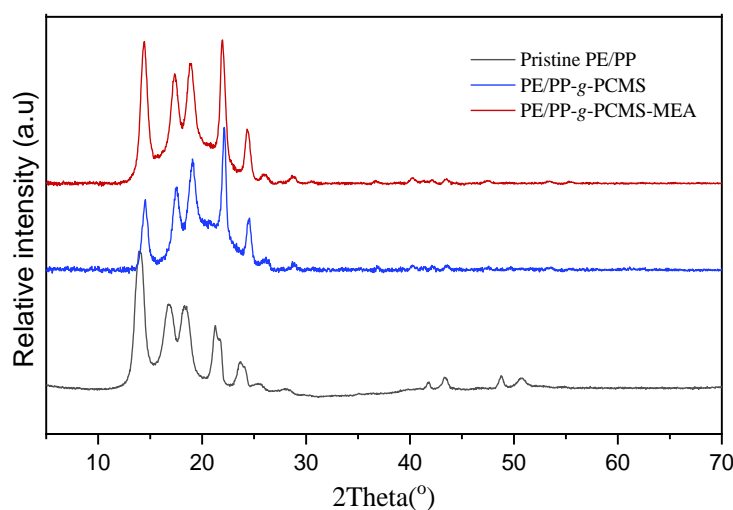
The molecular structure of pristine PE/PP PCMS-grafted and MEA-loaded samples were studied using Fourier transform infrared spectroscopy (FTIR) analysis as presented in Figure 2. The spectrum of pristine PE/PP polymer structure was marked by 2 peaks of antisymmetric and asymmetric stretching

vibrations of  $-\text{CH}_2$  at 2917 and 2847  $\text{cm}^{-1}$  [23]. The characteristics peaks at 838, 702 and 676  $\text{cm}^{-1}$  from the *p*-substituents on the aromatic ring together with the peaks at 1264  $\text{cm}^{-1}$  representing the  $-\text{C}-\text{Cl}$  groups and this clearly prove successful grafting of PCMS chains [22]. Furthermore, the appearance of the peak at 1527  $\text{cm}^{-1}$  was assigned for primary amine from MEA, which provide a prove of a successful amine loading [24].



**Figure 2.** FTIR spectra of pristine PE/PP (black), PE/PP-g-PCMS (blue) and PE/PP-g-PCMS-MEA (red)

Figure 3 shows XRD diffractograms of pristine PE/PP, PE/PP-g-PCMS and PE/PP-g-PCMS-MEA samples. The XRD measurements were carried out to observe the changes in the crystallinity of pristine PE/PP after incorporation of PCMS, which was followed by functionalization with MEA. The position of the peaks occurred at the same angle ( $2\theta$ ), indicating that the structure of pristine PE/PP was well preserved even after grafting and amination procedures [25]. However, all peaks have minor shifts to higher angles suggesting minor changes in the crystal sizes after the grafting and amination. This also proves that the aminated PCMS ligands were introduced to the amorphous regions of PE/PP in a way that led to no significant contribution to the diffraction pattern. [26].



**Figure 3.** XRD results for pristine PE/PP (black), PE/PP-g-PCMS (blue) and PE/PP-g-PCMS-MEA (red)

### 3.2 Effect of variation of monoethanolamine concentration

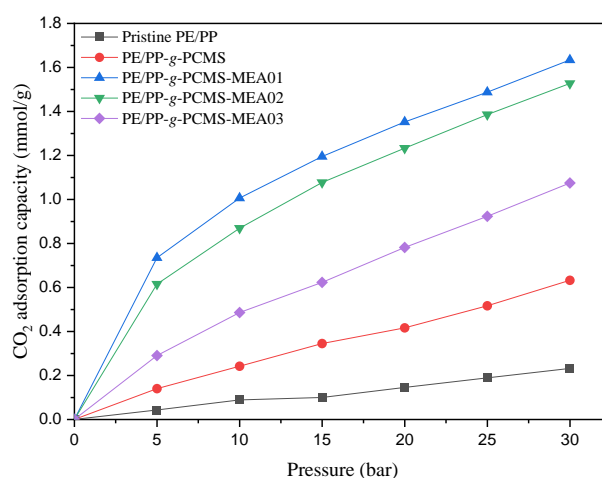
The effect of MEA concentration on the percent of amination can be seen in Table 1. The MEA concentration that was varied from 50% to 100% aqueous solutions led to an increase in percent of amination from 50 to 71%. This could be attributed to the increase frequency of efficient collisions between amine molecules and methyl chloride from PCMS ligand due to increased concentration of amine molecules in the solution [17]. The presence of a higher content of amine groups was predicted to have a higher CO<sub>2</sub> adsorption capacity due to strong affinity to CO<sub>2</sub> molecules.

**Table 1.** Percent of amination when treated with different concentration of MEA

Sample	Degree of grafting, DG (%)	Solvent	Concentration of MEA (%)	Percent of amination (%)
PE/PP-g-PCMS-MEA01	137	-	100	71
PE/PP-g-PCMS-MEA02	137	water	80	58
PE/PP-g-PCMS-MEA03	137	water	50	50

### 3.3 CO<sub>2</sub> adsorption on adsorbents with various MEA contents

The prepared fibrous adsorbent containing MEA was tested for CO<sub>2</sub> adsorption by using gravimetric sorption system at elevated pressure as presented in Figure 4. The results showed an increasing CO<sub>2</sub> adsorption capacity trends with the increase in the pressure for all samples with pristine PE/PP and PE/PP-g-PCMS as the reference. Similar trend was reported in literature for another amine-modified adsorbent [27,28]. This is due to the diffusion effect, where the high pressure pushed the CO<sub>2</sub> molecules to have more contact/access to amine sites and enhanced the adsorption capacity [29]. To evaluate the effect of amine content on CO<sub>2</sub> adsorption capacity, three samples of different amine contents: PE/PP-g-PCMS-MEA01, PE/PP-g-PCMS-MEA02 and PE/PP-g-PCMS-MEA03 that were prepared by treated using different concentrations of MEA as presented in Table 1. The CO<sub>2</sub> adsorption capacity showed that amination of PE/PP substrates increase the CO<sub>2</sub> adsorption capacity by 159% for MEA01, 143% for MEA02 and 70% for MEA03. A similar adsorption increasing trend with the increase in MEA concentration in a sequence of MEA01 > MEA02 > MEA03 and capacity of 1.63, 1.53 and 1.07 mmol/g at pressure 30 bar, respectively. These results suggest that the higher amine content gives higher CO<sub>2</sub> adsorption capacity. This is going along with previous observations made on similar fibers with higher content of primary amine confirming that faster adsorption rates and higher adsorption capacities take place with high amine contents [30].



**Figure 4.** CO<sub>2</sub> adsorption capacity at different pressure for pristine, grafted and aminated PE/PP

#### 4. Conclusion

The effect of MEA amine concentration on the CO<sub>2</sub> adsorption capacity of aminated PCMS containing fibrous adsorbent was successfully carried out. The percent of amination obtained from the experimental work showed that the higher concentration of MEA gives a higher yield of loaded amine with the rising trend in the order of 50% < 80% < 100% with amination percent as follows, 50%, 58% and 71, respectively. The obtained adsorbents demonstrated an increasing CO<sub>2</sub> adsorption capacity values of 1.63 mmol/g for MEA01, 1.53 mmol/g for MEA02 and 1.07 mmol/g for MEA03 at pressure 30 bar. The sample with the adsorption capacity of 1.63 mmol/g has a strong potential for future application in CO<sub>2</sub> removal after conducting the necessary kinetics, thermodynamics and stability investigations.

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